

UNITED STATES PATENT APPLICATION FOR:

ELECTROPLATING SOLUTION COMPOSITION CONTROL

INVENTORS:

RAJEEV BAJAJ
RAMIN EMAMI
GIRISH DIXIT
HIRAL AJMERA
ROMAN MOSTOVOY

ATTORNEY DOCKET NUMBER: AMAT/6298/CPI/ECP/PJS

CERTIFICATION OF MAILING UNDER 37 C.F.R. 1.10

I hereby certify that this New Application and the documents referred to as enclosed therein are being deposited with the United States Postal Service on 2-11-02, in an envelope marked as "Express Mail United States Postal Service", Mailing Label No. EL 913563835 US, addressed to: Assistant Commissioner for Patents, Box PATENT APPLICATION, Washington, D.C. 20231.

Burt Muccari
Signature
Burt Muccari
Name
2-11-02
Date of signature

ELECTROPLATING SOLUTION COMPOSITION CONTROL

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention generally relates to a method and apparatus for removing degraded additives from an electroplating solution.

Description of the Related Art

[0002] Electroplating processes for manufacturing semiconductor devices typically require a thin, continuous, electrically conductive seed layer to be deposited on the substrate prior to the plating process. The seed layer is generally formed of a conductive metal, such as copper, and is conventionally deposited on the substrate using PVD or CVD techniques. Electroplating a desired metal over the seed layer is then generally accomplished by applying an electrical bias to the seed layer and exposing the substrate to an electroplating solution containing metal ions that will plate over the seed layer in the presence of the electrical bias.

[0003] Copper has a lower resistivity, e.g., $1.7 \mu\Omega\text{-cm}$ compared to $3.1 \mu\Omega\text{-cm}$ for aluminum, and can carry a higher current density than aluminum. Therefore, it is generally desirable to use copper to form interconnects in semiconductor devices, rather than aluminum. Conventional copper electroplating solutions typically consist of copper sulfate, sulfuric acid and additives to aid in depositing copper on the surface of a substrate and in filling sub-micron sized features, e.g., vias and interconnects. The additives may include any combination of, but not limited to, levelers, brighteners, inhibitors, suppressors, enhancers, accelerators, and surfactants. The additives are typically organic molecules that adsorb onto the surface of the substrate. Certain additives may decrease the ionization rate of metal atoms, thereby inhibiting the deposition process, whereas other additives may increase the deposition rate of metal ions.

PATENT

Attorney Docket No.: AMAT/6298/CPI/ECP/PJS

Express Mail No.: EL913563835US

[0004] However, a problem encountered in utilizing conventional electroplating processes is that organic additives degrade over time as a result of the application of an energy source to the electroplating solution, *e.g.*, electrical current, light, and as a result of chemical interactions. The degradation of organic additives generally increases as the plating current increases. As such, conventional processes typically overcome additive degradation by adding fresh additives to the electroplating solution. The amount and timing of the fresh additive addition is generally dependent on costly chemical analysis that continuously measures the concentration of additives in the electroplating solution. Chemical analysis systems generally include many sensors for monitoring plating conditions within the solution. The sensors typically detect additive degradation, thereby indicating the additional amount of additive to be added to the solution. Although, chemical analysis is necessary to monitor traditional electroplating solutions, the analysis is not always accurate by the time the results are available, as the additives are continuously degrading.

[0005] In addition, although the fresh additive restores the additive concentration in the electroplating solution, a substantial portion of the degraded additives remain in the solution, thereby building up, and potentially reducing plating performance. Although the effect of organic buildup on plating performance is unknown, it is believed that the initial organic compositions are altered by chemical interactions. Therefore, it is desirable to limit organic buildup in electroplating solutions. As a result, traditional systems remove a portion of the electroplating solution based on time and plating usage, *e.g.*, up to 25 percent of the solution per day. Additional electroplating solution is then added to restore the solution volume.

[0006] Therefore, there exists a need for a method and apparatus for removing degraded additives from electroplating solutions within an electroplating system.

SUMMARY OF THE INVENTION

[0007] Embodiments of the present invention generally relate to an apparatus for depositing a metal layer onto a substrate, including an electrochemical deposition

PATENT

Attorney Docket No.: AMAT/6298/CPI/ECP/PJS

Express Mail No.: EL913563835US

cell having an electrolyte inlet in fluid communication therewith, an electrolyte fluid reservoir in fluid communication with the electrochemical deposition cell via a fluid delivery conduit, and at least one activated carbon filter in fluid communication with the fluid delivery conduit, the at least one activated carbon filter being configured to have an affinity for degraded organic plating additives.

[0008] Embodiments of the present invention further relate to a method for removing degraded organic additives from an electroplating solution. The method generally includes capturing at least a portion of an electroplating solution stream traveling between an electroplating fluid reservoir and an electroplating deposition cell, and flowing the captured portion of electroplating solution through an activated carbon filter having an affinity for plating solution organic additives.

[0009] Embodiments of the invention further relate to a method for depositing metal on a substrate. The method generally includes providing a substrate having a seed layer disposed on a surface thereof, disposing the substrate in an electroplating solution, and flowing at least a portion of the electroplating solution through an activated carbon filter. The at least a portion of the electroplating solution is a fluid volume sufficient to remove an amount of organic additives from the electroplating solution that is equal to a calculated rate of organic additive degradation. The method further includes flowing the electroplating solution to the substrate.

[0010] Embodiments of the invention further relate to a method for removing degraded organic additives from an electroplating solution stream traveling between an electroplating fluid reservoir and an electroplating deposition cell. The method is generally accomplished by flowing a portion of electroplating solution through an activated carbon filter having an affinity for plating solution organic additives, so that the organics may be removed therefrom.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] So that the manner in which the above recited features of the present invention are attained and can be understood in detail, a more particular description

of the invention, briefly summarized above, may be had by reference to the embodiments thereof, which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention, and are therefore, not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0012] Figure 1 is a perspective view of an exemplary electroplating system of the invention.

[0013] Figure 2 is a sectional view of an exemplary electroplating cell of the invention.

[0014] Figure 3 is an illustration of organic additive degradation in a conventional electroplating system.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0015] Figure 1 is a perspective view of an electroplating system 100 including a mainframe 114, an electroplating solution replenishing system 120, and a control system 122. The mainframe generally includes a thermal anneal chamber 111, a loading station 110, a spin rinse dry station 112, and a plurality of processing stations 118. The loading station 110 generally includes one or more substrate cassette receiving areas 124, generally known as pod loaders, one or more loading station transfer robots 128, and at least one substrate orientor 130. Each processing station 118 includes one or more processing cells 140.

[0016] The control system 122, may be a programmable microprocessor configured to interface with the various components of the system 100 and provide controlling signals thereto. The electroplating solution replenishing system 120 is generally positioned adjacent the electroplating system 100 and in fluid communication with the process cells 140 in order to circulate electroplating solution to the cells 140.

PATENT

Attorney Docket No.: AMAT/6298/CPI/ECP/PJS

Express Mail No.: EL913563835US

[0017] Figure 2 is a cross sectional view of an exemplary electroplating cell of the present invention. The electroplating process cell 200 may be implemented into system 100. The exemplary processing cell 200 generally includes a head assembly 210, a process kit 220, and an electroplating solution collector 240. Preferably, the electroplating solution collector 240 is secured onto the body 242 of the mainframe 114 over an opening 243 that defines a location for placement of the process kit 220. The electroplating solution collector 240 generally includes an inner wall 246, an outer wall 248, and a bottom 247 connecting the respective walls. A drain 249 may be disposed through the bottom 247 of the electroplating solution collector 240 and may be in fluid communication with, for example, the electroplating solution replenishing system 120.

[0018] An electroplating solution 274 is disposed in the electroplating solution collector 240 and generally flows through a drain 249 into a reservoir 270. A pump (not shown) then recycles the electroplating solution 274 through a fluid delivery conduit 278 back to the electroplating solution collector 240. The electroplating solution 274 may also be transferred from the reservoir 270 through the fluid delivery conduit 278 to the electroplating solution replenishing system 120 for additive replenishment, and then back to the electroplating solution collector 240.

[0019] The electroplating solution 274 may be an aqueous solution and may contain sulfuric acid, phosphoric acid, or derivatives thereof. The electroplating solution 274 may further include one or more organic additives. Additives, for example, levelers, inhibitors, suppressors, accelerators, brighteners, or other additives known in the art, are typically organic materials that adsorb onto the surface of the substrate being plated. Useful suppressors typically include polyethers, such as polyethylene, glycol, or other polymers such as polypropylene oxide, which inhibit the rate copper deposition on the substrate. Useful accelerators typically include sulfides or disulfides such as bis(3-sulfopropyl) disulfide, which affect the microstructure of copper deposited on the substrate. Useful levelers typically include amines or polyamines, which improve the thickness distribution of copper deposited on the substrate.

PATENT

Attorney Docket No.: AMAT/6298/CPI/ECP/PJS

Express Mail No.: EL913563835US

[0020] In specific embodiments of the invention, the electroplating solution 274 is disposed in the electroplating solution collector 240 and generally flows through the drain 249 into the reservoir 270. A filter 272 is generally disposed between the reservoir 270 and the inlet to electroplating solution collector 276 to remove organic additives from the electroplating solution 274. The filter 272 can alternatively be placed between the drain 249 and the reservoir 270, or elsewhere in the system 100.

[0021] In an exemplary embodiment of the invention, the filter 272 is disposed in a recovery stream 280 located downstream of the reservoir 270 and upstream of the inlet to the electroplating solution collector 276 to remove the degraded organics before they enter the electroplating solution collector 240. All, or a portion, of the electroplating solution 274 may flow from the reservoir 270 through the filter 272 via the recovery stream 280. The electroplating solution 274 flows from the filter 272 to the electroplating solution replenishing system 120 to determine the necessary replenishment of organic additives and the filter's 272 effectiveness. The electroplating solution 274 then flows back to the reservoir 270. The electroplating solution 274 not flowing through the recovery stream 280 flows to the inlet 276.

[0022] Embodiments of the invention further contemplate that the volume of electroplating solution 274 flowing through the filter 272 may be equal to a calculated value, such as an observed additive degradation rate. Figure 3 illustrates degradation rates in conventional systems. As shown, the degradation rate is generally known to vary depending on the individual additive. The degradation rate also varies based on the age of the electroplating solution 274 and the electrical current supplied to the cell 200. The calculated rate of organic additive degradation generally correlates to the amount of electroplating solution 274 that is removed from the plating system 100 per day, *i.e.*, in a 24 hour period. The rate of organic additive degradation may also be calculated as a function of current and time, therefore the degradation rate will vary depending on the specifics of an electroplating system. For example, the degradation rate may be about 2 percent to about 10 percent over 200 amp hours. The calculated rate of additive degradation is

PATENT

Attorney Docket No.: AMAT/6298/CPI/ECP/PJS

Express Mail No.: EL913563835US

generally between about 2 percent and about 10 percent of the total additives in the electroplating solution 274 per 24 hour period. Removing organic additives in a rate equal to the system rate of degradation may substantially reduce replenishment costs and the chemical analysis necessary to continuously determine the required addition of additives downstream of the filter 272. For example, if the calculated rate of organic degradation is about 5 percent of the total organic additives in the solution 274 in a given time period, *i.e.*, a 24 hour period, an amount of electroplating solution 274 sufficient to remove 5 percent of the organic additives from the entire electroplating solution 274 may be passed through the filter 272 via the recovery stream 280 to remove the organics in the recovery stream 280, *i.e.*, 5% of the total organics in the solution 274. Based on the calculated rate of degradation, which corresponds to the volume flowing through the filter 272, 5 percent of the organic additives will be replenished downstream of the filter 272 in the electroplating solution replenishing system 120. As a result of filtering, organic additive analysis is generally unnecessary after each pass through the filter 272.

[0023] The filter 272 may include any substance capable of capturing organics from the electroplating solution 274. The filter 272 may consist of activated carbon, for example. Two such filters are commercially available under the trade names Penguin series PC and Penguin style M from KTH Sales, Inc., located in Merrillville, Indiana. The filter effectiveness may vary for each organic component in the electroplating solution. As used herein, "effectiveness" refers to the percent of organics removed from the recovery stream 280, *i.e.*, total effectiveness is equal to 100 percent of the organics being removed from the recovery stream 280. The filter 272 may remove anywhere from about 14 percent to about 95 percent of the organic additives in the electroplating solution 274, depending on system requirements. The filters used in embodiments of the invention generally remove from about 60 percent to about 95 percent of the organic additives in the recovery stream 280. Effectiveness is also a function of the flowrate of the electroplating solution 274 flowing through the filter 272. When the electroplating solution 274 flows through the filter 272 at a high flowrate, for example from about 4 gpm to about 7 gpm, less organic additives are removed than are removed when the electroplating solution

PATENT

Attorney Docket No.: AMAT/6298/CP/ECP/PJS

Express Mail No.: EL913563835US

274 is flowing at a lower flowrate. The effectiveness is further defined based on the number of passes of the electroplating solution through the filter 272. Although a particular filter may only have a single pass effectiveness of about 3 percent to about 10 percent, the filter's overall effectiveness may be increased by increasing the number of passes through the filter. Embodiments of the invention may pass a volume of electroplating solution 274 through the filter 272 a number of times equal to the number of passes necessary to achieve an overall effectiveness of about 60 percent to about 95 percent per day.

[0024] The rate of organic additive degradation may vary over time. For example, the initial amount of degraded additives in the electroplating solution 274 will be less than the amount of degraded additives in the electroplating solution 274 after plating 1,000 substrates. Therefore, the rate of organic removal in the filter 272 and organic replenishment, may increase over time. The rate of electroplating solution 274 flowing through the filter 272, i.e., the recovery stream 280, may be controlled by a control valve 282. The control valve 282 may be controlled by a system controller that processes data received by organic analysis. Based on that data, the rate of electroplating solution 274 flowing through the filter 272 may be increased or decreased to filter an amount of electroplating solution 274 sufficient to remove organic additives from the electroplating solution 274 in an amount equal to the calculated amount of degraded organic additives in the solution 274.

[0025] Various configurations of the electroplating solution replenishing system 120 may be employed. For example, two or more filters may be situated in parallel or in series depending on the needs and demands of the system. Additionally, three filters 272 may be situated in parallel to allow for varying capacities of electroplating solution 274. For example, one filter 272 may be used when 2 percent of the electroplating solution 274 is passing through the filter 272, while three filters 272 may be used when 70 percent of the electroplating solution 274 is passing through the filters 272.

[0026] In the embodiments described herein, the filter 272 has an affinity for organics. Thus, all, or a substantial portion, of the organics are removed from the

PATENT

Attorney Docket No.: AMAT/6298/CP/ECP/PJS

Express Mail No.: EL913563835US

electroplating solution 274 as the solution 274 flows through the filter 272. As a result, the rate of organic additive degradation in the solution 274 is reduced without the need to treat the solution 274 with hydrogen peroxide, *i.e.*, to breakdown organic additives, prior to passing the solution 274 through the filter 272.

[0027] After a period of use, the filter 272 may be replaced. Preferably, the filter 272 is replaced when the electroplating system 100 is serviced, for example, every 50,000 substrates. Although the filter 272 is preferably replaced at service, the filter 272 may be replaced at any point, which is economically feasible.

[0028] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.